HYDROGEN BOND STUDIES

112. Molecular Reorientations in some Hydrogen Bonded Solids

by

Rolf Sjöblom

Doctoral Dissertation

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Abstract

Proton magnetic resonance second moments and relaxation times at various temperatures are reported for tri- and dimethylammonium iodide, bromide, chloride and hydrogen oxalate, and for most of the twenty common amino acids. A general procedure is described for the calculation of theoretical second moments and relaxation times in dipolar solids. In several cases, this procedure is applied to determine the molecular reorientations present as well as the corresponding activation barriers. The results are discussed with particular reference to hydrogen bonding.

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To Margareta, Lilly and Fritz

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Abstract

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The thesis comprises this summary and the following articles:

R. Sjöblom and J. Tegenfeldt, *Acta Chem. Scand.* **26**, 3068 (1972). Hydrogen Bond Studies 63. A nuclear Magnetic Resonance Study of Molecular Motion in Solid Dimethylammonium Chloride.

R. Sjöblom and J. Tegenfeldt, *Acta Chem. Scand.* **26**, 3075 (1972). Hydrogen Bond Studies 64. A Proton Magnetic Resonance Study of Molecular Motion in Solid Trimethylammonium Chloride.

R. Sjöblom and J. Tegenfeldt, UUIC-B13-2, Institute of Chemistry, University of Uppsala (1973). A computer program for the calculation of theoretical second moments of NMR spectra from solids in the presence of molecular reorientations.

R. Sjöblom and J. Tegenfeldt, *J. Magn. Res.* **20**, 0000 (1975) in press. Hydrogen Bond Studies 107. A Proton Magnetic Resonance Study of Molecular Motion in Solid Trimethylammonium Iodide, Bromide and Hydrogen Oxalate.

R. Sjöblom and M. Punkkinen, *J. Magn. Res.* **20**, 0000 (1975) in press. Hydrogen Bond Studies 108. A Proton Magnetic Relaxation Study of Molecular Motion in Solid Trimethylammonium Iodide, Bromide, Chloride and Hydrogen Oxalate.

R. Sjöblom, UUIC-B19-137, Institute of Chemistry, University of Uppsala (1975). A General Procedure for the Calculation of Theoretical Nuclear Magnetic Resonance Second Moments and Relaxation Times in Dipolar Solids; Applications to Oxalic Acid Dihydrate and the Trimethylammonium Ion.

R. Sjöblom, UUIC-B19-135, Institute of Chemistry, University of Uppsala (1975). Hydrogen Bond Studies 114. A Wide-Line and Pulse Proton Magnetic Resonance Study of Molecular Motion in Solid Dimethylammonium Chloride.

R. Sjöblom, UUIC-B19-136, Institute of Chemistry, University of Uppsala (1975). Hydrogen Bond Studies 115. A Wide-Line and Pulse Proton Magnetic Resonance Study of Molecular Motion in Solid Dimethylammonium Iodide, Bromide and Hydrogen Oxalate.

E.R. Andrew, W.S. Hinshaw, M.G. Hutchins and R.O.I. Sjöblom, UUIC-B-19-139, Institute of Chemistry, University of Uppsala (1975). Proton Magnetic Relaxation and Molecular Motion in Polycrystalline Amino Acids I. Aspartic Acid, Cystine, Glycine, Histidine, Serine, Tryptophan and Tyrosine.

E.R. Andrew, W.S. Hinshaw, M.G. Hutchins, R.O.I. Sjöblom and P.C. Canepa, UUIC-B19-140, Institute of Chemistry, University of Uppsala (1975). Proton Magnetic Relaxation and Molecular Motion in Polycrystalline Amino Acids II. Alanine, Isoleucine, Leucine, Methionine, Norleucine, Threonine and Valine.

E.R. Andrew, W.S. Hinshaw, M.G. Hutchins and R.O.I. Sjöblom, UUIC-B19-141, Institute of Chemistry, University of Uppsala (1975). Proton Magnetic Relaxation and Molecular Motion in Polycrystalline Amino Acids III. Arginine, Asparagine, Cysteine, Glutamine, Phenylalanine and Proline.

R. Sjöblom, UUIC-B13-7, Institute of Chemistry, University of Uppsala (1975). Some computer programs using a general procedure for the calculation of NMR second moments and relaxation times in dipolar solids.

CONTENTS

1. General introduction

1.1 *The hydrogen bond project*

Hydrogen bonding plays an important role in many inorganic, organic and biological systems. It is, for instance, believed that nearly all biochemical processes at some stage involve the breaking and forming of hydrogen bonds.

Studies concerning the fundamental properties of hydrogen bonding are carried out within the *hydrogen bond project* (HBP) in Uppsala under the leadership of Professor Ivar Olovsson. As a result, 115 publications have to date appeared in the series entitled *hydrogen bond studies* (HBS), ten of which are doctoral theses[1–10]. The work carried out before 1975 has recently been summarized in Ref. 11.

The following methods have been used in the project: X-ray and neutron diffraction, vibrational spectroscopy, nuclear magnetic resonance and quantum chemical calculations. The investigations have, with few exceptions, been carried out in the solid state.

1.2 *The hydrogen bond*

A detailed description of the various aspects of hydrogen bonding falls outside the scope of this summary; such information is contained within Refs. 12 to 17. Instead, a few remarks will be made with particular reference to the hydrogen bond project.

A typical hydrogen bond X—H · · · Y between two molecules may be regarded as a result of three types of interaction[8,16]: (a) the *electrostatic interaction* between the unperturbed electron and nuclear charge distributions of the free molecules, (b) the *polarisation* of the molecules (the redistribution of charges) due to the electrostatic interactions, and (c) the *recombination of the molecular orbitals* causing covalency in the H · · · Y bond and a change in the covalency of the X—H bond.

The model one should use in practice depends, of course, on the particular experiment. One could perhaps say that, in general, a model involving (a), or (a) and (b) may be sufficient for weak and intermediately strong hydrogen bonds while consideration of all three types of interaction is required for strong bonds. This view is supported by numerous theoretical calculations as discussed in Refs. 8 and 16.

The electrostatic energy varies relatively slowly with the distance between the molecules. For condensed phases it is important to take the electrostatic field of the surroundings into consideration.

In a hydrogen bond X—H · · · Y, the positively charged atom H is attracted by the negative acceptor atom Y, while the negatively charged donor atom X is repelled from it. The electrostatic energy for this part of the system thus has its minimum for a linear bond. X-ray and neutron diffraction experiments have provided clear evidence

indicating that most hydrogen bonds tend to be close to linear[6,17]. These experiments have also shown that the H · · · Y distance is usually considerably shorter than the sum of the van der Waals radii of the atoms H and Y, indicating the presence of polarisation or polarisation and covalency. Quite recently, the diffraction technique has been developed to produce maps of essentially the valence electron density. These are in good agreement with those obtained from theoretical *ab initio* calculations (see, for example, Ref. 18).

Several other techniques have also been used in order to study hydrogen bonding: frequencies and intensities of certain infrared, far infrared and Raman bands can be related to the properties of the X—H and H · · · Y bonds, and the changes in polarisation during vibration, respectively[19].

Quadrupole coupling constants[19] (related to the gradients of the electric fields at the sites of the nuclei), chemical shifts[16], and activation barriers to molecular reorientations can be determined by nuclear magnetic resonance and are also sensitive to the hydrogen-bond interactions. It has been shown[20] that the X—H distance, the infrared frequency (mainly associated with stretching of the X—H bond) and the quadrupole coupling constant of the hydrogen atom are well inter-correlated. Consequently, any of these three quantities could, at least in principle, be taken as an indicator of "hydrogen-bond strength". Another such indicator is the dissociation energy which, together with the reorientational barrier, will be discussed in the next section.

1.3. *Molecular reorientations*

The qualitative picture of how the energy varies with the H · · · Y distance in a linear hydrogen bond between two uncharged molecules is similar to that for other bonds (see, for example, Ref. 14). It is well known that the associated potential well contains vibrational states, and that the dissociation energy is the difference between the energy at infinite separation and that of the lowest vibrational level[21]. Dissociation energies are directly related to the relative stability of different complexes and can also be used to estimate the rates of breaking and forming of hydrogen bonds. The dissociation energy in the gas phase is mainly associated with the hydrogen bond interactions described in the previous section (1.2).

During a molecular reorientation in a solid hydrogen bonds are sometimes broken, at least partially. In such cases, the reorientation barrier can be regarded as one counterpart to the dissociation energy in the gas phase. The hindered rotation of NH_3-groups is one type of molecular motion studied in this thesis. Here the groups undergo torsional oscillations about their three-fold pseudo-symmetry axes. Occationally the NH_3-groups become sufficiently thermally activated to overcome the reorientation barrier, so causing a permutation of the hydrogen atoms. In some cases (*cf.* the motion of dimethylammonium ions discussed later in this summary) the motion of

one group may strongly affect the potential experienced by another group. Such effects can give rise to cooperative motion.

The reorientation barrier depends on the electrostatic, the van der Waals and hydrogen bond interactions which, in turn, depend on the changes in geometry occurring during the reorientation. It has been found, for instance, that the activation barrier for a reorientation of an NH_3-group in monomethylammonium chloride changes drastically from about 32 to 4 kJ/mole on passing through the γ to α phase transition[5,22]. The hydrogen-bond strength, as indicated by infrared data, is approximately the same in the two phases, however[22]. The low activation barrier in the α-phase is clearly related to the geometry of the environment: there are four chloride ions around each NH_3 rotor, arranged in such a way that the potential to reorientations of the groups becomes twelve-fold[22].

It is interesting to compare the characteristics of reorientational motion involving the breaking and forming of hydrogen bonds with those of ordinary chemical processes. The difference between the dissociation energy of such a bond in the gas phase and the corresponding reorientation barrier in a solid may be thought of as being caused by a form of catalysis or inhibition. The reorientation rate corresponds to the reaction rate, and the changes in geometry during a reorientation to the reaction coordinate. Furthermore, both the reorientation and the reaction rates often follow an Arrhenius type relation[23]: $\tau=\tau_0 \exp(E/RT)$.

2. Method

2.1 *Introduction*

There are several different mechanisms for interactions between the electric quadrupole and the magnetic dipole moments of a nucleus and its surroundings[24–28]. The present nuclear magnetic resonance investigations have (with one exception) involved only nuclei of normal hydrogen which possess no electric quadrupole moment. The nuclear magnetic dipole-dipole coupling has determined both the shape of the NMR line and the rate of dissipation of energy from the spin system to the thermal bath provided by the motions in the crystal. Only this type of interaction will therefore be discussed in the following.

The NMR line-shape is dependent on the crystal structure, the changes in geometry resulting form the molecular reorientations and the rates of the reorientations. The line-width changes when the reorientation rate (the inverse of the correlation time) becomes comparable with the line-width. The line-shape is, however, difficult to calculate theoretically[28] and, instead, the second moment (equal to one fourth of the mean-square line-width) is usually used.

The dissipation of energy from the spin system (comprising all nuclei at resonance) to the thermal bath provided by the motions in the crystal usually follows an exponential relation. The time-constant in the exponent, T_1 (the spin-lattice relaxation time), also depends on the crystal structure, the changes in geometry resulting from the molecular reorientations and the rates of the reorientations. The spin-lattice relaxation time has its minimum when the reorientation rate is of the same order of magnitude as the resonance frequency.

In NMR experiments of the present kind, the resonance frequency and the line-width are typically of the order of 10^7–10^8 and 10^4 Hz, respectively. These values may be compared with the frequencies relevant to other experimental techniques. In infrared spectroscopy and X-ray diffraction, for instance, the frequencies are typically of the order 10^{13} and 10^{18} Hz, respectively. Molecular reorientations usually occur at rates which are at least a few orders of magnitude slower than molecular vibrations, and thus fall in the range where the NMR technique is sensitive. NMR can thus be used to study the time-dependence of molecular reorientations. Furthermore, the second moments and relaxation times also depend on the geometries of the equilibrium configurations. This makes the NMR technique particularly well suited to the study of processes involving the breaking and forming of hydrogen bonds.

In systematic work of the present kind which involves the application of one technique to several compounds, it is important to optimize the procedures used for the recording of data and for their interpretation. A general procedure for the calculation of second moments and relaxation times has thus been developed[29]. The method is

briefly described in sections 2.2 (second moments) and 2.3 (relaxation times). The procedure has been included in several computer programs as summarized in section 2.4.

2.2 *Second moments*

The second moment of a dipolar solid depends on its crystal structure, the molecular reorientations and the direction of the external magnetic field according to the well-known Van Vleck formula[26,30]:

$$M_2 = M_{2l} + M_{2u}$$

where

$$M_{2l} = \frac{3}{4}\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{\infty}\gamma_j^4\hbar^2 I_j(I_j+1)\langle\langle b_{ij}\rangle^2\rangle$$

$$M_{2u} = \frac{1}{3}\frac{1}{N}\sum_{i=1}^{N}\sum_{k=1}^{\infty}\gamma_i^2\gamma_k^2\hbar^2 I_k(I_k+1)\langle\langle b_{ik}\rangle^2\rangle$$

$$\text{and } b_{ij} = \frac{3\cos^2\theta_{ij}-1}{r_{ij}^3}$$

The quantities M_{2l} and M_{2u} are the contributions from interactions between spins of the same and different kinds, respectively, r_{ij} is the distance between atoms i and j and θ_{ij} is the angle between the external magnetic field and the vector connecting the two atoms. N is the number of atoms at resonance per unit cell, and γ and I are the gyromagnetic ratio and spin for a nucleus. The inner average of b_{ij} is taken over all motions characterized by a correlation time sufficiently short to cause the maximum possible reduction of the second moment. The outer average takes account of static disorder, or of situations where the nuclear motions are slow compared to the NMR line-width.

The direct application of the Van Vleck formula often implies that tedious calculations involving summations over many pairs of nuclei have to be carried out many times[29]. For this and other reasons which will shortly become apparent (*cf.* sections 2.2, 2.3 and 2.4). Van Vleck's formula has been rewritten in the following way[29]:

$$M_2 = \tilde{\mathbf{q}}\mathbf{S}\mathbf{q}$$

Here M_2 is the second moment, **q** is a vector containing five elements which only depend on the direction of the external magnetic field, and **S** is a symmetric 5 x 5

second moment tensor which depends only on the crystal structure and the motions present. The second moment tensor need thus be calculated only once for each particular situation; the second moment for any orientation can then readily be obtained using the above formula.

The restrictions imposed on the elements of the second moment tensor by the symmetry of the crystal are given in Table 3 of Ref. 29. These relations are helpful in the determination of theoretical and experimental second moment tensors and can also, in many cases, be used to determine the orientation of a single crystal.

Particular simplifications arise when the second moment averaged over the motion of a rigid body is to be calculated. In this case **S** (motion) $= \widetilde{\mathbf{T}}$ **S** (rigid) **T**, where **T** depends only on the unitary transformations associated with the reorientations of the rigid body.

A similar formula can be used for calculations of the second moment reduced by rigid body vibrational motion (which usually causes the largest vibrational alteration of the second moment in molecular solids). The intra-rigid body second moment (the effect of the vibrations are usually much smaller for the inter-rigid body second moment) is given by the formula **S** (vibration) $= \widetilde{\mathbf{T}}$ **S** (rigid) **T**, where **T** in this case is related to the librational tensor in a simple way[29].

Further advantages in using the second moment tensor appear when an average is to be taken over the orientations of the crystallites in a powder. Here the second moment is simply the trace (the sum of the diagonal elements) of the second moment tensor.

2.3 *Relaxation times*

Relaxation times in the laboratory and rotating frames, T_1 and $T_{1\rho}$, can, for any direction of the external magnetic field, be calculated from the second moment tensors if the correlation times of the different motions are known[29]. (Several underlying assumptions here are discussed in Ref. 29). The following formulae are valid if the relaxation is caused by motions which have only a single correlation time:

$$T_1^{-1} = \frac{2}{3}\,\tilde{\mathbf{q}}\,\Delta\mathbf{S}^{(1)}\mathbf{q}\,\frac{\tau}{1+\omega_0^2\tau^2} + \frac{8}{3}\,\tilde{\mathbf{q}}\,\Delta\mathbf{S}^{(2)}\mathbf{q}\,\frac{\tau}{1+4\omega_0^2\tau^2}$$

and

$$T_{1\rho}^{-1} = \tilde{\mathbf{q}}\,\Delta\mathbf{S}^{(0)}\mathbf{q}\,\frac{\tau}{1+4\omega_1^2\tau^2} + \frac{5}{3}\,\tilde{\mathbf{q}}\,\Delta\mathbf{S}^{(1)}\mathbf{q}\,\frac{\tau}{1+\omega_0^2\tau^2} + \frac{2}{3}\,\tilde{\mathbf{q}}\,\Delta\mathbf{S}^{(2)}\mathbf{q}\,\frac{\tau}{1+4\omega_0^2\tau^2}$$

together with $\tau=\tau_0 \exp(E/RT)$, where E is the activation barrier associated with the motion, τ is the correlation time, τ_0 is the time factor, ω_0 is the resonance frequency, and ω_1 is the Larmor frequency in the rotating frame. $\Delta\mathbf{S}^{(0)}$, $\Delta\mathbf{S}^{(1)}$ and $\Delta\mathbf{S}^{(2)}$ are interrelated by simple transformations given in Table 8 in Ref. 29, and $\Delta\mathbf{S}^{(0)}=\mathbf{S}$(rigid)$-$ **S** (motion). Thus, second moments and relaxation times are closely related, and both methods can be used to determine differences between second moment tensors. The symmetry restrictions on **S** also apply for $\Delta\mathbf{S}^{(0)}$, $\Delta\mathbf{S}^{(1)}$ and $\Delta\mathbf{S}^{(2)}$. The relaxation times for a powder are also given by the above formulae if $\mathbf{q}\,\Delta\mathbf{S}^{(m)}\mathbf{q}$ is replaced by $\mathrm{Tr}\,\Delta\mathbf{S}^{(m)} = \mathrm{Tr}\,\Delta\mathbf{S}^{(0)}$.

In order to account for molecular vibration the second moment tensors in the above formulae need only be replaced by vibrationally averaged ones (which can be obtained as described in the preceding section (2.2)).

Similar but slightly more complex formulae have been derived for cases where several types of motion take place simultaneously but independently of one another, as described in Ref. 29.

2.4 *Computer programs*

The procedure for the calculation of second moments and relaxation times outlined above has been included in several computer programs. PSM[31,32] calculates second moment tensors from the known crystal structure and molecular reorientations. SMP[32] calculates the second moment from the second moment tensor and the direction of the external magnetic field relative to the crystal. ESM[32] is a least-squares program which simultaneously refines the elements of the second moment tensor and the orientations associated with up to five single crystal mountings using experimental second moments. Constraints in symmetry and orientation can be included in the refinements in a flexible way.

The relaxation time, T_1, can readily be evaluated from the experimental data using the program TON[32] which is based on a least-squares procedure. The program ACT[32] and derivatives of it determine the time factor, τ_0, the activation barrier, E, and the relaxation constant, C ($=2/3\ \mathrm{Tr}\,\Delta\mathbf{S}^{(0)}$), in a powder for up to five motional processes in a least-squares procedure using experimental relaxation times.

2.5 *Experimental*

The spectra from which the second moments were extracted were obtained using continuous wave NMR spectrometers with separate coils for transmitting and receiving the radio-frequent oscillations of the magnetic field[24]. About half of these measurements have been performed in Uppsala on a Varian Inc. NMR spectrometer. The other measurements have been made on similar instruments at the University of Not-

tingham and at the University of Florida.

The relaxation times have been determined using 180°–90°, 90°–90° or saturation sequence –90° pulses on a variable frequency Bruker 322s pulse NMR spectrometer at the University of Nottingham. In all cases, except for about half of the amino acids studied, the relaxation times were evaluated from the experimental data using the program TON[32].

The temperature was measured to an accuracy of ±2 K using thermocouples. The orientations of single crystals were determined in least-squares procedures using about ten reflexions in each case on a four-circle X-ray diffractometer.

3. Results and conclusions

3.1 *Trimethylammonium iodide, bromide, chloride and hydrogen oxalate*

The compounds trimethylammonium iodide, bromide, chloride and hydrogen oxalate will in the following be denoted by TMAI, TMAB, TMAC and TMAHOX. At 308 K β-TMAC transforms to α-TMAC in going from low to high temperature[33]. TMAI[34], TMAB[34], β-TMAC[35] and TMAHOX[36] all crystallize in the space group $P2_1/m$ but the packing is different except for TMAI and TMAB which have similar structures[34]. The crystal structure of α-TMAC[4,37] is tetragonal, space group $I4/mmm$.

The experimental second moment *vs.* temperature curves for these compounds[34,38,39] exhibit values at the lowest temperatures which are in agreement with values calculated for rigid structures. The second moments decrease in the region 120 to 220 K and are essentially constant between 220 and 350 K. The second moments at the latter plateaus indicate that the methyl groups as well as the cations as a whole reorient about their respective three-fold pseudo-symmetry axes (*cf.* Fig. 1). Similar situations have also been observed in other trimethylammonium and trimethylamine compounds. It has therefore been suggested[5,39] that the motions of the methyl groups and the cations as a whole may be coupled. Relaxation studies (to be described shortly) have shown that the two motions do not have the same correlation time over any appreciable temperature interval in any of the four compounds studied. This indicates that the motions cannot be completely correlated.

The relaxation time *vs.* temperature curves for TMAI, TMAB, β-TMAC and TMAHOX have features indicating that more than one kind of reorientation take place[40]. Expressions for the relaxation time as a function of the distance between the

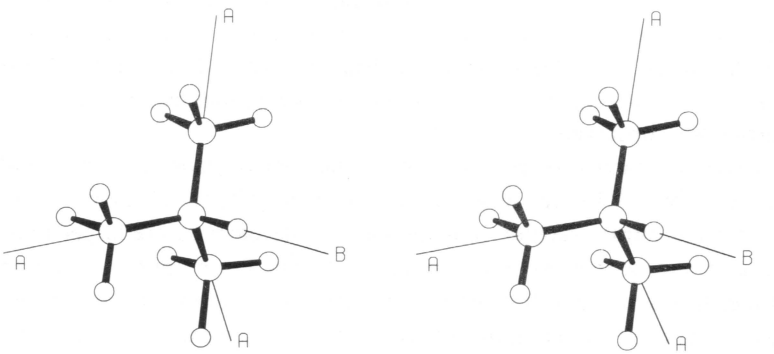


Figure 1. A stereoscopic drawing of the trimethylammonium ion showing (A) the three-fold reorientation axes of the methyl groups and (B) the three-fold reorientation axis of the cation as a whole.

Table 1. The experimental activation barriers (in kJ/mole) for reorientations of the methyl groups (motion A) and of the cations as a whole (motion B) about their respective three-fold pseudo-symmetry axes (*cf.* Fig. 1) in the trimethylammonium salts studied.

Compound and phase	motion	
	A	B
TMAI	18.7	33
TMAB	22.1	42
β-TMAC	19.3	38
α-TMAC	13.4	–
TMAHOX	18.6	27

methyl groups (actually the corresponding relaxation constants were refined), the activation barriers and the time factors of the two processes were derived[40] using a method described in Ref. 41. Two models were used in the least-squares refinements of the above parameters from the experimental relaxation times: (a) the motions are independent and (b) the motions are correlated in such a way that the methyl groups reorient freely during a reorientation of the cation as a whole. Both models gave equally good agreement between observed and calculated relaxation times. Furthermore, the parameters obtained using the two models agreed to within about three times their combined standard deviations. It was therefore concluded that the parameters are insensitive to the detail of the frequency spectrum, and that model (a) may be preferred on grounds of simplicity. The activation barriers determined in refinements according to model (a) are shown in Table 1. The same results (as for model (a) above) would have been obtained by using the procedure described in Ref. 29.

The reorientation rate for motions of the cations as a whole is rather high in α-TMAC and consequently only the reorientations of the methyl groups contribute to the observed relaxation (*cf.* Table 1)[40]. The barrier to reorientations of the cations as a whole should thus be rather small. This can be related to the symmetric environment of the cation in α-TMAC which implies a twelve-fold barrier[4,37]. The situation here is similar to that of the α-phase of monomethylammonium chloride where a very low barrier was observed[5,22].

The activation barrier to reorientations of the methyl groups in TMAI, TMAB, β-TMAC and TMAHOX are of about the same magnitude (*cf.* Table 1), which indicates that the intramolecular contributions to the barriers are larger than the intermolecular and/or that the intermolecular barriers are of approximately the same magnitude. As discussed in Ref. 40, an estimate of the intermolecular part of the barrier may be obtained by taking the difference between the barriers in the β- and the α-phases of TMAC; this gives a value of 6 kJ/mole. The barriers to reorientation of the cations as a whole vary more than those of the methyl groups (*cf.* Table 1); this is only to be expected since the packing is different in the different compounds.

The reorientation of the cations as a whole roughly about the N-H directions (*cf.* Fig. 1) can be related to two features: (a) the strongest interaction between the trimethylammonium ion and its surroundings is the N–H · · · Y hydrogen bond, and (b) the ion has three-fold pseudo-symmetry about this direction.

3.2 *Dimethylammonium iodide, bromide, chloride and hydrogen oxalate*

The compounds dimethylammonium iodide, bromide, chloride and hydrogen oxalate will in the following be denoted by DMAI, DMAB, DMAC and DMAHOX. All exhibit different crystal structures, cells and symmetries[42–45]. Furthermore, DMAB exhibits two phases[42], and DMAC[33,46] and DMAHOX[42] each three phases.

The dimethylammonium ion has C_{2v} symmetry and is thus less symmetric than the trimethylammonium ion which has C_{3v} symmetry. The molecular reorientations immediately suggested by this symmetry and the shape of the ion are (A) reorientations of the methyl groups about their three-fold pseudo-symmetry axes, and (B) reorientations of the cation as a whole about the two-fold symmetry axis (*cf.* Fig. 2). This axis is associated, however, with a considerably higher moment of inertia than an axis parallel to the carbon-carbon direction which passes through the centre of mass (model C in Fig. 2). Reorientations about this latter axis must therefore also be considered.

The γ-phase of DMAC is stable at low temperature and transforms at 260 K to β-DMAC which, in turn, transforms to α-DMAC at 313 K[33,46]. The crystal structure of γ-DMAC is not known, but the structures of β-DMAC[43] (*cf.* Fig. 3) and α-DMAC[44] have been determined by X-ray diffraction. The α-phase is disordered and the average structure observed consists of a superposition of the various asymmetric units in β-DMAC[44]. Infrared data on the α- and β-phases indicate that the short-range structure of the α-phase is similar to that of the β-phase[44]. One would therefore

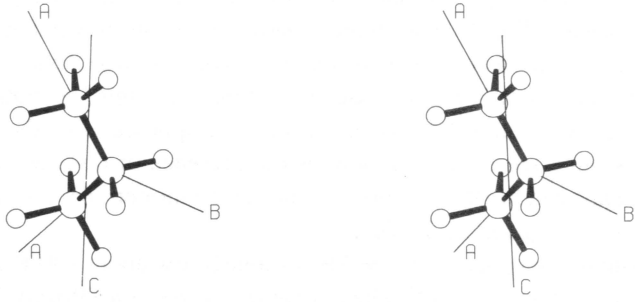


Figure 2. A stereoscopic drawing of the dimethylammonium ion showing (A) the three-fold reorientation axes of the methyl groups, (B) the two-fold reorientation axis of the cation as a whole and (C) the essentially four-fold reorientation axis of the cation as a whole.

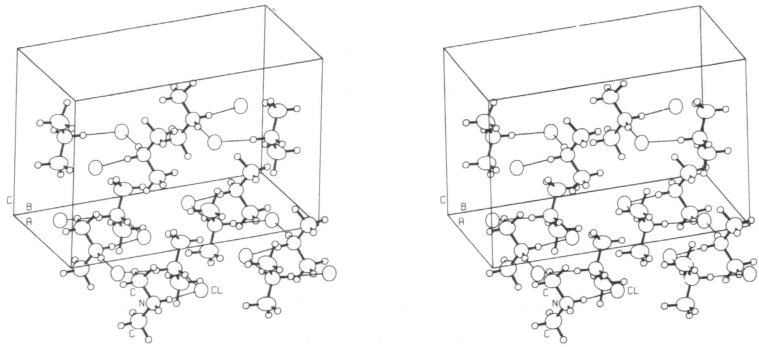


Figure 3. A stereoscopic drawing of the crystal structure of β-DMAC. The hydrogen bond chains are parallel to the crystallographic *a*-axis.

expect that motion (C) takes place in the α-phase (see below) if the disorder is dynamical.

DMAC has been the subject of several NMR investigations: second moments[38,47] and relaxation times[48] have been determined for polycrystalline samples as a function of temperature, and the quadrupole coupling constant and the asymmetry parameter at room temperature have been determined for the deuterons bonded to nitrogen[47]. Furthermore, second moments as a function of orientation have been determined in the α- and β-phases for two single crystals[48]. The following conclusions were drawn from these experiments:

Only the methyl groups reorient in γ-DMAC (model A above). Motions (A), (B) and (C) above (*cf.* Fig. 2) take place in the β-phase. Motion (C), however, is only consistent with the observed X-ray structure (*cf.* Fig. 3) if these motions take place in a highly correlated way so that the translation symmetry is preserved within most of the mosaic blocks. This suggests that there exist boundaries of disordered structure which move around in the crystal[47,48]. A part of the structure originally exhibiting the arrangement shown in Fig. 4a would thus, after some time, exhibit any of the four arrangements shown in Fig. 4. (The changes between the four possibilities in Fig. 4 are actually not equivalent; this problem is treated and discussed in Refs. 47 and 48). The same motions take place in the α-phase. The correlation time for motion (B) is here longer than that for motion (C), while the opposite appears to be the case in the β-phase. This is quite reasonable in view of the presence of disorder in the α-phase which can be expected to affect motion (C) more than motion (B). The activation barriers determined are given in Table 2.

DMAB exhibits two phases: β-DMAB is stable below about 180 K and α-DMAB is stable above this temperature[42]. The crystal structures of α-DMAB, β-DMAB and DMAI have not been determined, but those of α-DMAB and DMAI are known to be different since the unit cells and Laue symmetries are different[42].

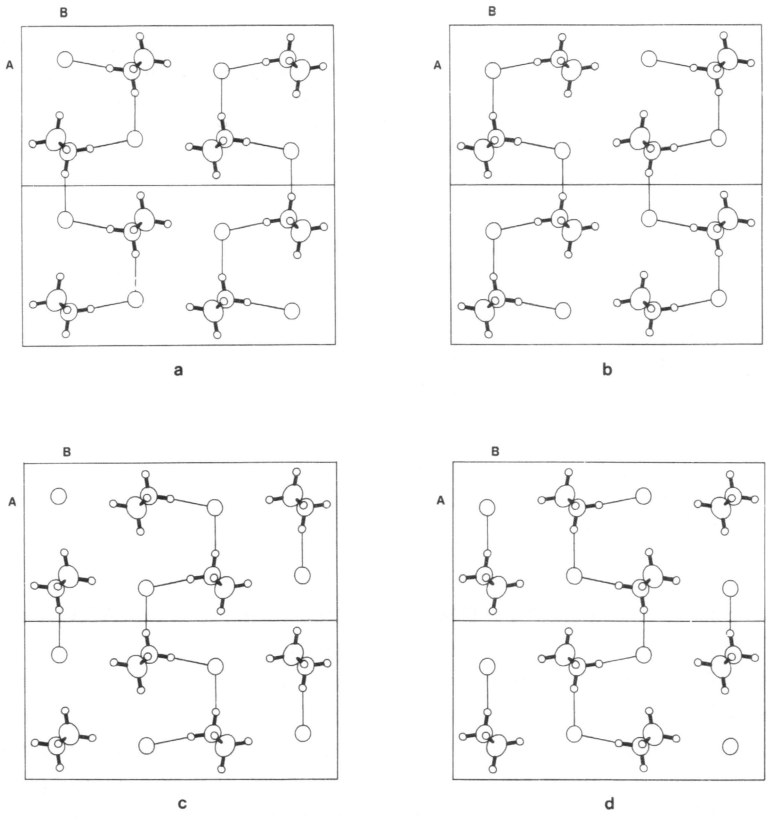


Figure 4. The motion (C) in the β-phase of DMAC implies that the structure changes between the configurations a, b, c and d. The layers above and below (*cf.* Fig. 3) have been assumed to change correspondingly.

Proton magnetic resonance second moments and relaxation times of polycrystalline samples have been determined as a function of temperature[42]. Comparisons between experimental and theoretical values of second moments and relaxation constants have shown that the methyl groups and the cations as a whole reorient (*cf.* Table 2), and that the reorientation rate associated with the former motion is much higher than that of the latter. The large similarities between the experimental second moments of DMAI and β-DMAB and those of DMAC indicate that the motions of the cations may well be rather similar in the three compounds. Further single crystal X-ray and/or NMR data are, however, required before any detailed conclusions can be drawn concerning these motions.

DMAHOX exhibits three phases: γ-DMAHOX is stable below room temperature and β-DMAHOX at temperatures above room temperature; the transition between

Table 2. The experimental activation barriers (in kJ/mole) for molecular reorientations in the dimethylammonium salts studied. The motions are (*cf.* Fig. 2): (A) reorientations of the methyl groups about their three-fold pseudo-symmetry axes, (B) reorientations of the cations as a whole about their two-fold pseudo-symmetry axes, and (C) reorientations of the cations as a whole about axes parallel to the carbon-carbon directions (and close to the centres of mass). The labelling "cation" refers to cases where the detailed motion of the cations as a whole could not be determined.

Compound and phase	motion			
	A	B	C	cation
DMAI	16.9			57
β-DMAB	17.0			
α-DMAB	18.5			62
γ-DMAC	14.7			
β-DMAC	11.1			
α-DMAC		42	23	
γ-DMAHOX	17.4			
β-DMAHOX	10.2			75
α-DMAHOX				49

these two phases is hindered[42]. γ-DMAHOX transforms to α-DMAHOX at about 330 K[42]. The crystal structure of only the γ-phase is known[45].

γ-DMAHOX exhibits reorientations of only its methyl groups, as confirmed by PMR second moments and relaxation times[42] (*cf.* Table 2). Relaxation data on β- and α-DMAHOX indicate that the methyl groups as well as the cations as a whole reorient; the former at a much higher rate than the latter. It would again appear that single crystal X-ray and/or NMR data are required before conclusions can be drawn concerning the details of the motions of the cations as a whole.

It is interesting to note that the dimethylammonium ion reorients as a whole in at least one of the phases of each of the compounds studied (*cf.* Table 2). These motions involve the breaking and forming of N–H · · · Y hydrogen bonds. The activation barriers here (*cf.* Table 2) are accordingly higher than those obtained for the trimethylammonium ion (*cf.* Table 1) which reorients about its pseudo-symmetry axis and thus maintains its hydrogen bonding during a reorientation.

The barriers to methyl group reorientation in the dimethylammonium compounds range between 10 and 19 kJ/mole (*cf.* Table 2). These are somewhat smaller than those obtained for the trimethylammonium compounds which range between 13 and 22 kJ/mole (*cf.* Table 1). This difference may be expected since a neighbouring hydrogen atom represents less steric hinderance than a methyl group.

It may also be of interest in this context to make a comparison with the reorientation barriers for the methyl groups is gaseous monomethylamine[49] (8.3 kJ/mole), dimethylamine[50] (13.5 kJ/mole) and trimethylamine[51] (18.4 kJ/mole) which were determined by microwave spectroscopy. The substitution of a methyl group for a hydrogen atom thus results in an increase in the barrier of about 5 kJ/mole.

3.3 *Amino acids*

The amino acids are very important in most biological systems and have consequently drawn the attention of many scientists. Structural data from X-ray and/or neutron diffraction are thus available for most of them (for further references see Ref. 9 and 17). Several NMR investigations of solid amino acids have also been carried out; these are compared with the present investigations in Refs. 52, 53 and 54 where, in most cases, it is concluded that the agreements are reasonable.

Measurements have been made of the spin-lattice relaxation time of protons in most of the twenty common amino acids encountered in proteins[52–54]. The specimens were in polycrystalline form and were studied in the temperature range 130–500 K. The results have been analyzed (*cf.* chapter 2 and Ref. 29) using the expression

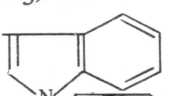
$$T_1^{-1} = \sum_i C_i \left(\frac{\tau_i}{1 + \omega_0{}^2 \tau_i{}^2} + \frac{4\tau_i}{1 + 4\omega_0{}^2 \tau_i{}^2} \right)$$

together with $\tau_i = \tau_{0i} \exp(E_i/RT)$, where C_i is the relaxation constant, τ_i the correlation time, τ_{0i} the time factor and E_i the activation barrier for process i. Table 3 shows the values of the activation barriers obtained from the non-linear least-squares refinement (*cf.* section 2) using the experimentally determined relaxation times.

The amino acids studied exhibit one or two minima in a plot of relaxation time against temperature. Numerous diffraction experiments have shown that most of the amino acids occur in their zwitterion form, $^+H_3HCHGCOO^-$, where G is a side group. All compounds which are known to contain an NH_3-group have a high temperature minimum, and those which also contain a methyl group have an additional low temperature minimum. Most of the minima were indeed shown to be caused by reorientations of these groups using the following approaches: (a) comparisons between experimental and theoretically calculated relaxation constants, (b) comparison between experimental and theoretically calculated second moments, and (c) selective deuteration on the amino nitrogen[52–54]. The observed T_1 minima for methyl groups in L-valine and DL-leucine seem insufficiently deep to be caused by reorientations of all methyl groups. Additional minima may therefore be expected at lower temperatures for these compounds. The crystal structure of L-valine indicates that there are four structurally inequivalent (but chemically equivalent) methyl groups in each asymmetric unit. This suggests that there are, in principle, four minima caused by the reorientations of the methyl groups (some of which may be superposed).

Theoretical calculations using the procedure described in Ref. 29 have shown that most of the contributions to the relaxation constant can be attributed to interactions from within the CH_3- and the NH_3-groups. One would here expect that the experimental relaxation constants are approximately inversely proportional to the number

Table 3. The experimental activation barriers (in kJ/mole) for the molecular reorientations in the amino acids studied.

Amino acids	Side chain	motion		
		CH_3	NH_3	other motions (*cf.* text)
L-alanine	$-CH_3$	22.4	38.6	
L-arginine	$-(CH_2)_3NHC(NH)NH_2$*			25.2, 35.7
L-asparagine	$-CH_2CONH_2$		32.3	
L-cysteine	$-CH_2SH$		37.1	10.6
L-cystine	$-CH_2SSCH_2-$		31.5	
L-glutamine	$-CH_2CH_2CONH_2$		32.6	
glycine	$-H$		28.6	
L-histidine	$-CH_2$ 		31.4	
L-isoleucine	$-CH(CH_3)CH_2CH_3$	13.0	44.8	
DL-leucine	$-CH_2CH(CH_3)_2$	13.2	51.7	
DL-methionine	$-CH_2CH_2SCH_3$	6.7	39.4	
DL-norleucine	$-(CH_2)_3CH_3$	12.6	41.7	
L-phenylalanine	$-CH_2$ 		51.2	18.2
DL-serine	$-CH_2OH$		40.0	
L-threonine	$-CH(CH_3)OH$	12.0	32.5	
L-tryptophan	$-CH_2$ 		27.8	
L-tyrosine	$-CH_2$  $-OH$		37.0	
L-valine	$-CH(CH_3)_2$	11.3	37.4	

* The arginine molecule actually occurs as $^{+}(NH_2)_2\ CNH(CH_2)_3\ CHNH_2COO^{-}$.

of protons relaxed by each such group. This relation is illustrated for NH_3-group reorientations in Fig. 5 where the points, as expected, approximately follow a straight line.

Only three cases of other types of motions arose. The curves for L-phenylalanine and L-cysteine show additional low temperature minima associated with comparatively small relaxation constants. These minima are probably caused by motions of the phenyl and SH groups, respectively. The shapes of the curves for L-arginine at two frequencies deviate from those expected for a single motional process, but a good fit was obtained in a refinement using parameters for two processes. It appears that the guanidinium group is protonated rather than the amino group since the relaxation constants differ by almost an order of magnitude from that expected for a reorienting NH_3-group.

The barriers hindering reorientations of the methyl groups (*cf.* Table 3) are closely

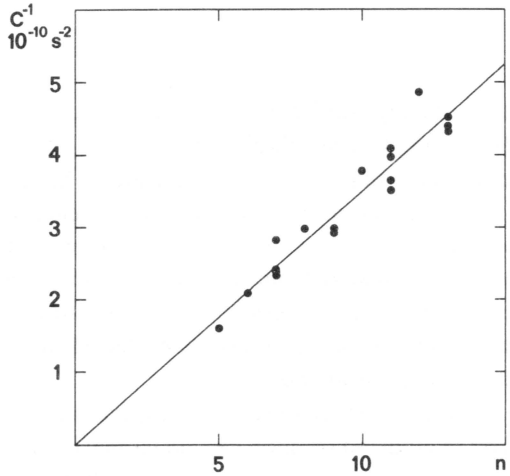


Figure 5. The variation of the inverse relaxation constant C^{-1} with the number of protons in the molecule for relaxation by NH_3-group reorientation.

similar (11.3—13.2 kJ/mole) except for L-alanine (22.4 kJ/mole) where the methyl group is close to the charged amino- and carboxyl-groups, and for DL-methionine (6.7 kJ/mole) where the methyl group is bonded to sulphur and thus has larger distances to neighbours. The relative constancy of the barriers suggest that they are largely intramolecular in origin and/or that the influence of the surroundings are very similar in the different compounds.

In contrast, the barriers to reorientation of the NH_3-groups vary considerably (between 27.8 and 51.7 kJ/mole, *cf.* Table 3). This suggests that the barriers are to a large extent intermolecular in origin, and depend on the details of the packing, hydrogen bonding and the electrostatic interactions. It appears that the barriers are somewhat higher for amino acids with hydrocarbon side-chains than for those whose side-chains contain other atoms as well (or contain no carbon atom at all). This may be explained as follows: Hydrogen-bond interactions are stronger than electrostatic interactions between other polar groups which, in turn, are stronger than the van der Waals interactions. If a hydrogen bond in a structure only competes with much weaker van der Waals interactions, one may expect an optimization of the hydrogen bond (it becomes strong, low in energy, linear, etc.). If, on the other hand, a hydrogen bond must compete with several electrostatic interactions, one may expect that a compromise is achieved so that the hydrogen bond becomes less well optimized (particularly less linear[6]) than in the former case. For an NH_3-group, the barrier to reorientation can be expected to be largest when the hydrogen bonds are linear, and to become much smaller if the bonds are considerably bent or bifurcated[5].

4. Summary

Processes involving the breaking and forming of hydrogen bonds are of great biological interest. The NMR technique is very well suited to the study of such phenomena accompanying molecular reorientations in the solid state. It has been shown that experimental data can readily be interpreted to yield the reorientations present as well as their respective activation barriers and reorientation rates, using a general procedure for the calculation of second moments and relaxation times.

The experimental studies have concerned some substituted ammonium compounds: tri- and dimethylammonium iodide, bromide, chloride and hydrogen oxalate, and most of the twenty common amino acids.

It was found that the methyl groups reorient comparatively rapidly in all cases. Their activation barriers to hindered rotation depend largely on the intramolecular interactions and are generally considerably smaller than those of hydrogen-bonded groups or molecules.

The trimethylammonium ions reorient as a whole about their three-fold pseudo-symmetry axes, and thus maintain their hydrogen bonding during these reorientations. The dimethylammonium ion also reorients as a whole in at least one of the phases in each of the compounds studied. It can undergo hindered rotations about both its two-fold pseudo-symmetry axis and about the axis of the smallest moment of inertia. In the β-phase of dimethylammonium chloride, this latter motion of the cation strongly affects its neighbours, so causing a remarkably strong correlation between the motions of neighbouring groups. The activation barriers to reorientations of dimethylammonium ions were, in most cases, larger than those of trimethylammonium ions, since hydrogen bonds are at least partially broken in the former but not in the latter case.

In the amino acids studied, all the NH_3-groups reorient about their three-fold pseudo-symmetry axes. The activation barriers range from 28 to 52 kJ/mole and depend on the hydrogen bonding (linearity), the electrostatic interactions and the packing.

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